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OPTICALLY ACTIVE DOPANTS INCORPORATING A 2,4-DISUBSTITUTED OXAZOLINE RING

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Abstract Novel optically active dopants for smectic C devices incorporating a 2,4-disubstituted oxazoline ring have been prepared from readily available starting materials. We report the observation of highly frustrated phase behaviour when these materials are added to a smectic C and nematic host, depending upon the degree of branching at the terminal chain adjacent to the chiral centre and the concentration of dopant used in the mixtures.

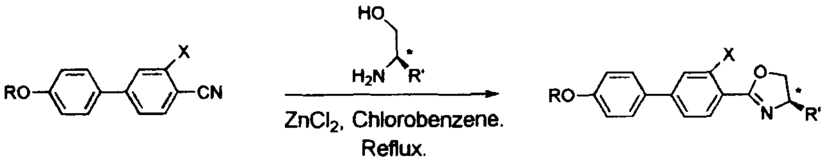
INTRODUCTION

Optically active dopants incorporating heterocyclic rings are of particular interest due to the presence of dipoles in the ring in close proximity to the chiral centre with a limited degree of intra-molecular rotation[1-7]. A limited number of mesomorphic 2,4-disubstituted oxazolines with liquid crystal cores and terminal branched alkyl chains at the chiral centre has been prepared and been reported in the literature[5-7]. These materials were synthesised for use as optically active dopants in chiral nematic and smectic C applications.

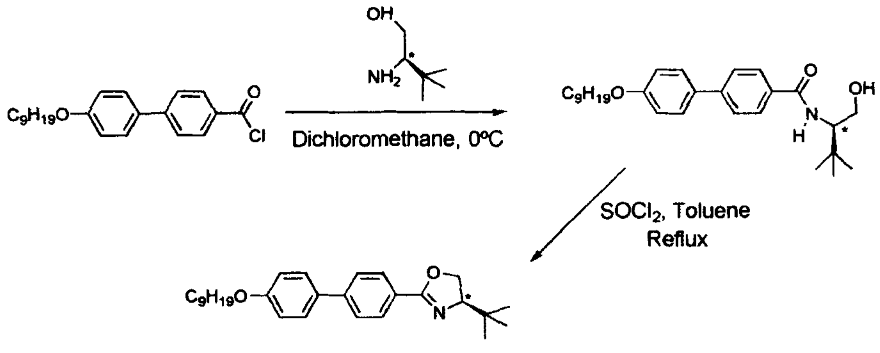
We decided to synthesise a number of 2,4-disubstituted oxazolines with either a non-branched or a branched chiral moiety as well as molecular cores of different conformational mobility in order to study their effect on the transition temperatures of the pure compounds and on the induced macroscopic chiral phases in mixtures. The 2,4-disubstituted oxazolines with non-branched terminal chains were expected to exhibit a greater tendency towards mesophase formation and higher transition temperatures in the pure state. They were also expected to lead to a lower depression of the chiral smectic C (S_C*) and nematic phase (N*) transition temperatures in mixtures. The oxazolines with a branched terminal chain could be expected to lead to lower transition temperatures in the pure state and in mixtures, but also to induce a higher degree of macroscopic chirality in mixtures because of steric effects.

Experimental

The desired 2,4-disubstituted oxazolines (**1-4**, **6-9**) were easily synthesised from readily available nitriles in a zinc catalysed cyclisation reaction[8] as shown in reaction Scheme 1 below. Compound 5 was synthesised from the acid chloride starting material *via* the chiral amide as shown in Scheme 2. The optically active 2-amino alcohols required were either commercially available or could be prepared from the corresponding amino acids by reduction with lithium aluminium hydride.



Scheme 1



Scheme 2

Transition Temperatures

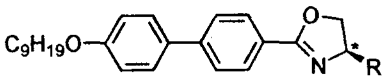
The thermal data in tables 1 and 2 for the fully aromatic (*S*)-2-(4'-alkoxy-biphenyl-4-yl)-4-alkyl-oxazolines (**1-9**) reveal that the smectic tendencies increase with the length of the terminal chain both at the chiral centre and attached to the aromatic core. A branched terminal chain suppresses mesomorphic behaviour as expected, see compounds (**3**, **4** and **5**). The presence of a lateral fluorine atom in the core of the compounds (**8** and **9**) also results in the suppression of the smectic phase observed for the corresponding non-fluorinated compounds (**6** and **7**), see table 2.

Physical Measurements

The oxazoline (**1**) was added in various concentrations to a non-optically active mixture, consisting of three difluoroterphenyls exhibiting nematic (N), smectic A (S_A) and smectic C (S_C) phases, in order to produce the chiral mixtures under investigation. The mixtures exhibit chiral nematic (N*), smectic A (S_A*) and smectic C (S_C*) phases. An unusual phenomenon observed for the mixtures with low dopant concentrations (<20%) is the observation of a twist grain boundary (TGB_A*) phase, although the pitch of the chiral dopant is relatively long in each case. TGB phases are normally associated with optically active compounds with a high molecular twisting power[9]. This suggests that the presence of the chiral centre in the core of the molecule leads to a greater interaction with the liquid crystal medium surrounding the dopant. At higher dopant concentrations (>50%) the dopant tends to crystallise out at relatively high temperatures and the transitions become broad with immiscibility regions. The mixtures with less dopant can be cooled to room temperature in the S_C* phase.

In order to study the effect of increasing the size of the substituent at the chiral centre in the moleular core, and thus increasing the helical twisting power, a similar series of mixtures was prepared using compound **5** as the dopant with a tertiary butyl group instead of an ethyl chain (see figure 1). It is proposed that the extremely bulky tertiary butyl group at the chiral centre induces even greater twisting into the system due to steric effects, evidence of which is provided by the wide range TGB phase (both thermally and by concentration) and the appearance of the blue phase (BP), another

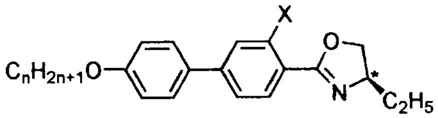
Table 1. Transition temperatures for the (*S*)-4-alkyl-2-(4'-nonyloxybiphenyl-4-yl)oxazolines (**1**-**5**) below.



Compound	R	C-S_2 /I /°C	S_2-I /°C	S_F-I /°C
1	C_2H_5	116	-	(<60)
2	iso-C_3H_7	102	-	-
3	n-C_4H_9	104	111	-
4	iso- C_4H_9	88	-	91
5	tert- C_4H_9	105	-	-

( ) Represents a monotropic transition temperature

Table 2. Transition temperatures for the (*S*)-2-(4'-alkoxybiphenyl-4-yl)-4-ethyl-oxazolines (**1**, **6** and **7**) and the (*S*)-2-(4'-alkoxy-3-fluorobiphenyl-4-yl)-4-ethyl-oxazolines (**8** and **9**) below.



Compound	n	X	C-I /°C	S_F-I /°C
1	9	H	116	(<60)
6	12	H	112	(108)
7	14	H	108	(104)
8	12	F	93	-
9	14	F	99	-

( ) Represents a monotropic transition temperature

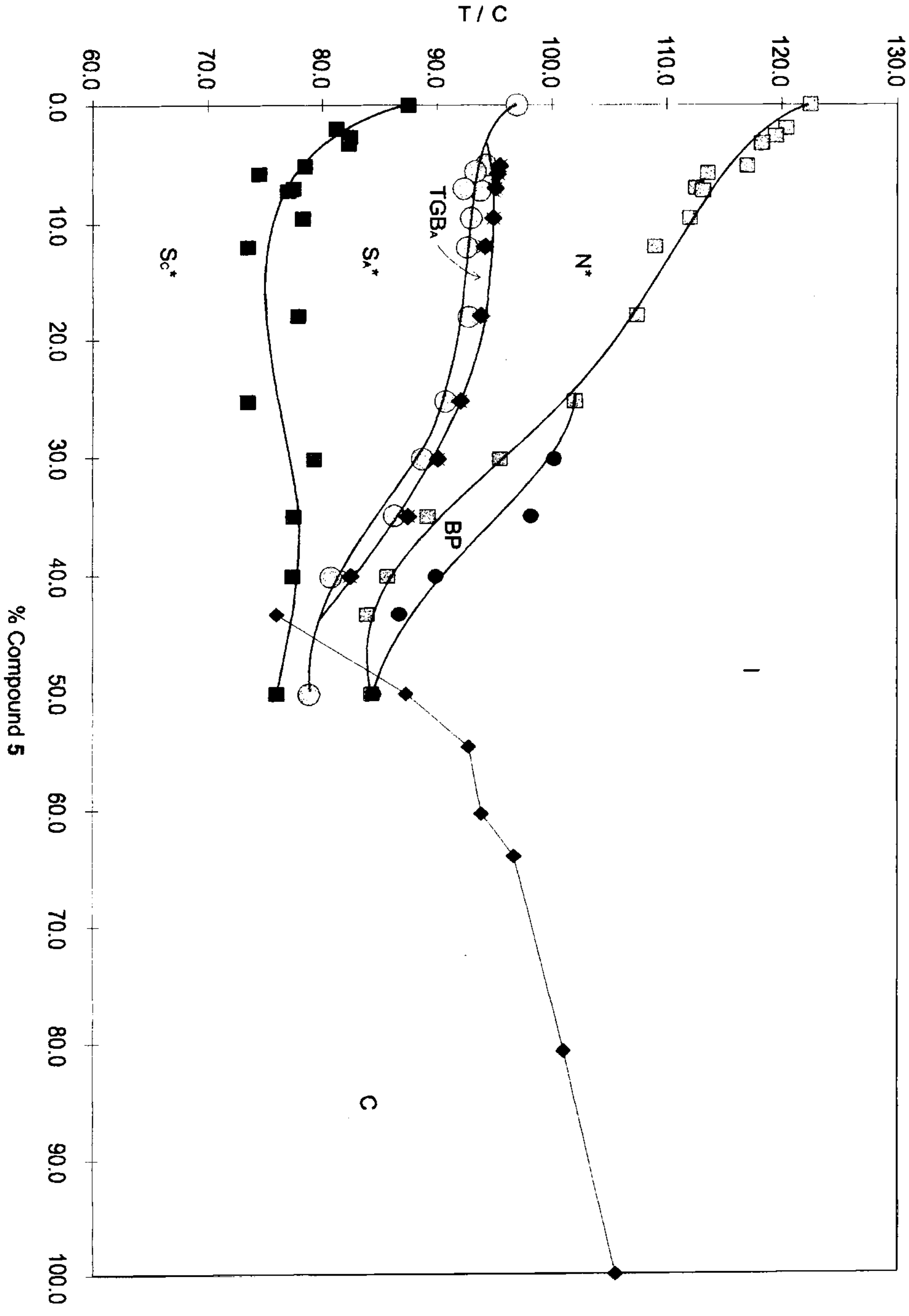

T / C
60.0
70.0
80.0
90.0
100.0
110.0
120.0
130.0
0.0
10.0
20.0
30.0
40.0
50.0
60.0
70.0
80.0
90.0
100.0
% Compound 5
N*
I
TGBA
SA*
SC*
BP
C

FIGURE 1

highly frustrated mesophase, at still higher concentration of dopant. Again, regions of immiscibility occur (>50% dopant concentration), and the mixture crystallises. However, the higher degree of chirality induced by the new dopant at high concentrations (>50%) where miscibility still occurs, induces such a small pitch that the helical S_C* phase is replaced by the alternating S_C*_A mesophase. This mesophase is observed over a very narrow temperature range due to the strong tendency for the mixture to crystallise at this temperature. The observation of this phase is, however, indicative of the high degree of molecular frustration within the system.

Although the P_S value of the chiral oxazoline dopant measured in the achiral smectic C matrix and extrapolated to 100% dopant concentration is found to be moderate, higher P_S values are observed for oxazolines with a second chiral centre in the terminal chain on the oxazoline ring or with internal hydrogen bonding[6].

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